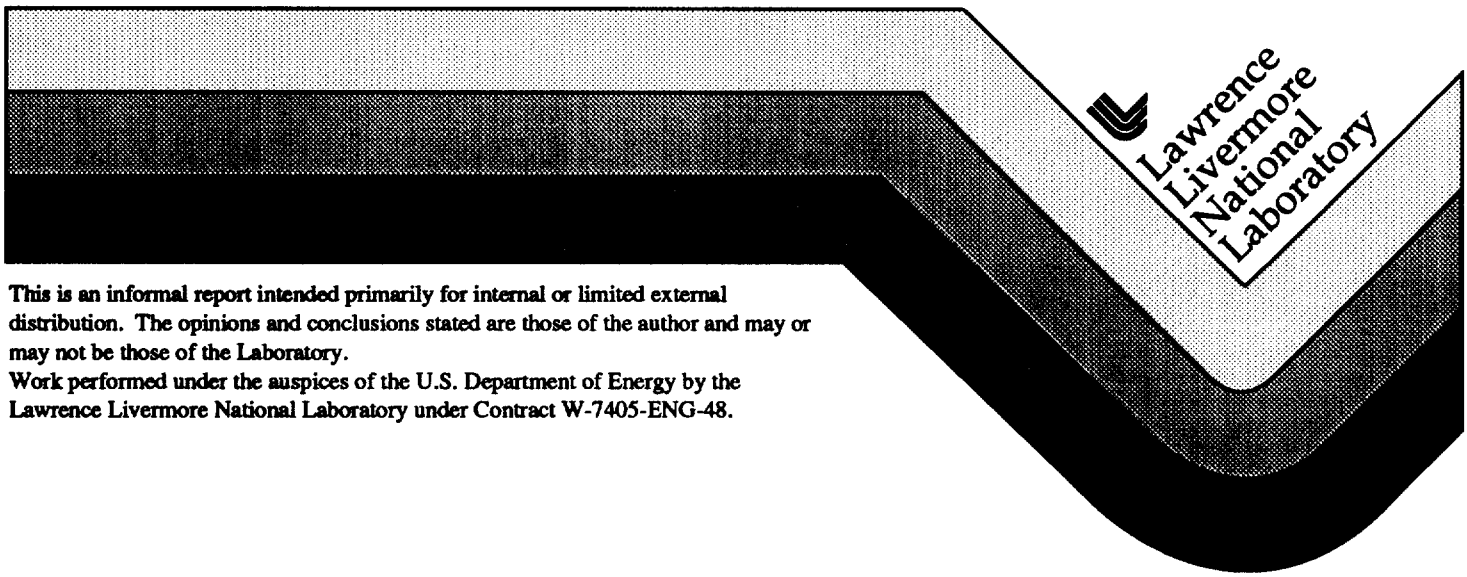
UCRL-ID-127172

Uranium Alloy Forming Process Research

T. S. Chow, T. A. Biesiada, A. Sunwoo, J. Long,
T. Anklam, S. W. Kang

March 1, 1997



Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

LDRD (96-ERD-016) Final Report

Uranium Alloy Forming Process Research

March 1997

Principal Investigator: T. S. Chow
L-Code: L-125
Email: chow4@llnl.gov
Tel: (510) 422-4639
FAX: (510) 423-4097

Co-Investigator: T. A. Biesiada
L-Code: L-460
Email: biesiada@llnl.gov
Tel: (510) 422-9258
FAX: (510) 423-1460

with support of

A. Sunwoo/DTED	Metallurgy
J. Long/ISAM	Metallurgy
T. Anklam /ISAM	Engineering
S. W. Kang/NTED	Modeling/KEM

Abstract

The study of modern U-6Nb processes is motivated by the needs to reduce fabrication costs and to improve efficiency in material usage. We have studied two potential options: (1) physical vapor deposition (PVD) for manufacturing near-net-shape U-6Nb, and (2) kinetic-energy metallization (KEM) as a supplemental process for refurbishing recycled parts. In FY 1996, we completed (1) two series of PVD runs and heat treatment analyses, (2) the characterization of the microstructure and mechanical properties, (3) a comparison of the results to data for wrought-processed material, (4) and experimental demonstration of the KEM feasibility process with a wide range of variables (particle materials and sizes, gases and gas pressures, and substrate materials), and (5) computer modeling calculations.

I. Description of Technologies and Goals

Physical Vapor Deposition (PVD)--This research examines the effects of PVD process variables and the supplemental process steps to validate the experimental findings already in hand and to improve the understanding of the microstructure characteristics of the PVD deposit. The goals are to lay a foundation for fabrication of hydro-test samples and to develop a PVD-based process for full scale manufacturing.

The key technical issues to be addressed are the improvement of composition homogeneity, and, consequently, control of the microstructure and mechanical properties of PVD material. The areas to be studied are the PVD process variables including ion bombardment during deposition, substrate temperature, and feed control; and subsequent material processing such as the optimization of heat treatment for the PVD material.

Kinetic Energy Metallization (KEM)--As a supplementary process for refurbishment/repair or creation of physical discontinuities for the blanks made by such process as PVD, the goal of this study is to establish feasibility using surrogate powder materials. An outside contractor (Innovative Technology Inc. (ITI)) is contracted to perform the experiments. As a background, ITI, who has the proprietary claim to the technology, first observed the KEM phenomena in a supersonic particle ignition study, and has since demonstrated its feasibility with a series of laboratory experiments. Typical process parameters to be

studied are: carrier gas type and pressure, powder materials (type and size), impact velocity, and target materials. Modeling will be included to enhance understanding of the process, and has been done under a separate funding source.

II. Project Plan

The project plan is summarized in the following table.

Deliverables	Objectives	Achievements
PVD		
• testing existing PVD samples from run #3	• build database and provide compare with wrought processed material • optimizing the process	• heat treatment • tensile tests • metallurgy • Auger scan • carbon analysis • deformation due to heat treatment: completed • shape memory: completed but results inconclusive • surface composition mapping
• PVD experiments	• process optimization for microstructure and properties including: substrate temperature, ion bombardment	• 5 Mars runs completed, 3 short-duration, two long-duration; 3 thick samples obtained: Mars #7- 700°C substrates temperature with enhanced ionization, and Mars #9- 600 and 700°C substrate temperatures with no ionization.
• testing new PVD samples		• #4-#6 samples optically micrographyed • #7 sample fully analyzed • #9 samples optically micrographed
KEM		
• deposition experiments consisting of parameters: powder material, substrate, powder size, gas pressure (100-450 psig), and gas: helium or nitrogen	• to demonstrate the KEM process feasibility	• KEM runs at ITI completed • mechanical test of KEM samples completed. • modeling using CALE computer code in progress, funded under other source
progress reporting		JOWOC31 meeting in May '96
process modeling and system analysis	cold and hot work process simulation	preliminary results
Reporting		reports and (refereed) Journal accepted

III. Accomplishments

We have accomplished the following:

- Completed 5 PVD runs to refine the process consisting of such parameters as substrate temperature, ion enhancement, and vapor flux density.
- Characterize microstructure and tensile properties of the samples from previous and most current runs.
- Compare the properties and characteristics of the PVD alloy with those from the conventional (wrought) processed alloy.
- KEM experiments and data analysis.
- Publications.

A.1 PVD Experimental Setup

The setup (Figure 1) consists of an electron beam gun; a bottom-fed water-cooled crucible; thermally controlled substrate(s); and a water-cooled vacuum chamber. The substrates were also electrically insulated so that a DC bias voltage could be imposed. In addition, a tantalum anode for ion-enhancement, and electrical hookup for the anode (500 amp at 30v) with electric insulation and grounding fixtures were also incorporated in the setup as shown for the current runs.

As the overhead E-beam melts the ingot from the crucible, the U and Nb vaporized and coated the substrates. Feedstock ingot was made by E-beam cold hearth melting and casting of U-6Nb forming scrap material. Since the scrap material was from a wrought-processed alloy, it is assumed that the ingot chemistry was within the specification of 5.2-6.5% wt-%Nb, and that there was no loss of Nb through vaporization process.

A.2 PVD Sample Analyses

The following table **(Table A1)** is a summary of (flat plate) runs from all Mars runs.

Table A1

Mars Runs #	temp °C	Bias KV	Gun Current, ampere	Vapor Rate, kg/hr	Ion %	Substrate	Comments and Notes
1	1050	0	4.0	4.7	0	aperture plate	pre-LDRD run: good properties, columnar grains, some banding
3	900	0	5.3	5.1	0	aperture plate	pre-LDRD run: good properties, columnar grains, micro-voids, banding
3	580	0.15-0.5	5.3	5.1	2	roof	pre-LDRD run: good properties, smaller, equiaxed grains, sharp banding
3	350	0.15-0.5	5.3	5.1	2	roof	pre-LDRD run: poor quality deposit
4							shakedown run for the current LDRD matrix
5	710	1.5	4.0	3.6	5	substrate	2 hour run: fully dense, smaller, equiaxed grains, very sharp banding
6	680	1.5	4.0	3.6	1	substrate	2 hour run: poor deposit
7	700	1.5	4.0	3.6	8	substrate	5-1/2 hour run: good tensile properties; some inclusions
9	580 & 700	0	5.5	6.6	0	roof and substrate	6 hour run: 2 solid deposits obtained (2-9/16"x5-3/16"x0.150") from substrates at 600 and 700°C, no bias nor ion enhancement; bias was lost due to shorting; the deposits on the roof substrates were poor. Metallurgy pending.

Testing of PVD Samples from Previous Runs (run #3) -- The heat treatment and mechanical testing of the PVD samples from run #3 run were completed. These samples were produced using two different substrate temperatures, 580°C with 0.15-0.5KV bias and 900 °C without bias (identified as PVD 500b and PVD 1000u, respectively), consisting of 8 specimens. The alloy made with the substrate

temperature at 580 °C has substantially better combined tensile properties than the one made with the substrate temperature at 900 °C. With aging at 200 °C for two hours, both sets of material showed a decrease in elongation but an increase in yield strength. However, at -40 °C, elongation for the 580 °C substrate material increased from 26% to 38%, as shown in **Table A2.**

The microstructure characterization showed that the grains of PVD 500b are equiaxed and about 10-20 μm in size with fine banding of Nb-rich regions and Nb-lean regions through the thickness. The microhardness trace across the bands indicates that the Nb-rich region is much softer than the Nb-lean region. Moreover, the size and volume fraction of the Nb-rich phase precipitates in PVD 500b are considerably different from those of the PVD 1000u. They were long and sparsely distributed in the uranium matrix, resulting in lower strength. Although the grains of PVD 1000u are columnar and an order of magnitude larger compared to PVD 500b, the Nb-rich phase precipitates are finely distributed in the uranium matrix, exhibiting higher strength and microhardness but lower elongation. In addition to the inverse relationship between the strength and the elongation, a lower elongation value is also attributed to the presence of voids along the boundaries. Because the material contains columnar grains, it may be quench sensitive, causing it to form voids along the boundaries to relieve thermal stresses. The causes of void formation will be further analyzed.

The tensile property values are compared with those of the wrought processed U6Nb alloy (Y-12) at room temperature and -40 °C. The wrought specimens were standard cylindrical geometry, whereas the PVD specimens were flat "dog-bone" shape, with a 40% reduced gage thickness to ensure failure in the gage length.

Table A2

Material ID	HT	Test (°C)	UTS (ksi)	YS (ksi)	Elongation (%)	E ($x10^6$ psi)
PVD 500b	γ-quench only	25	126	22	40	9
PVD 500b	γ-quenched and aged	25	130	51	26	9.9
PVD 500b	γ-quenched and aged	-40	150	51	38	10
PVD1000u	γ-quench only	25	144	28	24	10.6
PVD1000u	γ-quenched and aged	25	137	69	20	11.9
PVD1000u	γ-quenched and aged	-40	164	69	20	12
Wrought	γ-quenched and aged	25	126	65	34	10.5
Wrought	γ-quenched and aged	-40	148	67	33	11.1

Testing of PVD Samples from Current Runs (Mars #5, #6, #7, and #9) -- Metallurgic analyses of most of the samples have been competed showing: a solid deposit from #5 with sharp layers of banding, but a porous #6 deposit. Samples #7 and #9 were solid deposits thick enough for mechanical testing. #7 was obtained at 700°C with bias voltage at 0.15KV and enhanced ionization of 8%. #9 yielded two samples on separate substrates at 600 and 700°C with no bias. Analyses of #9 samples were incomplete.

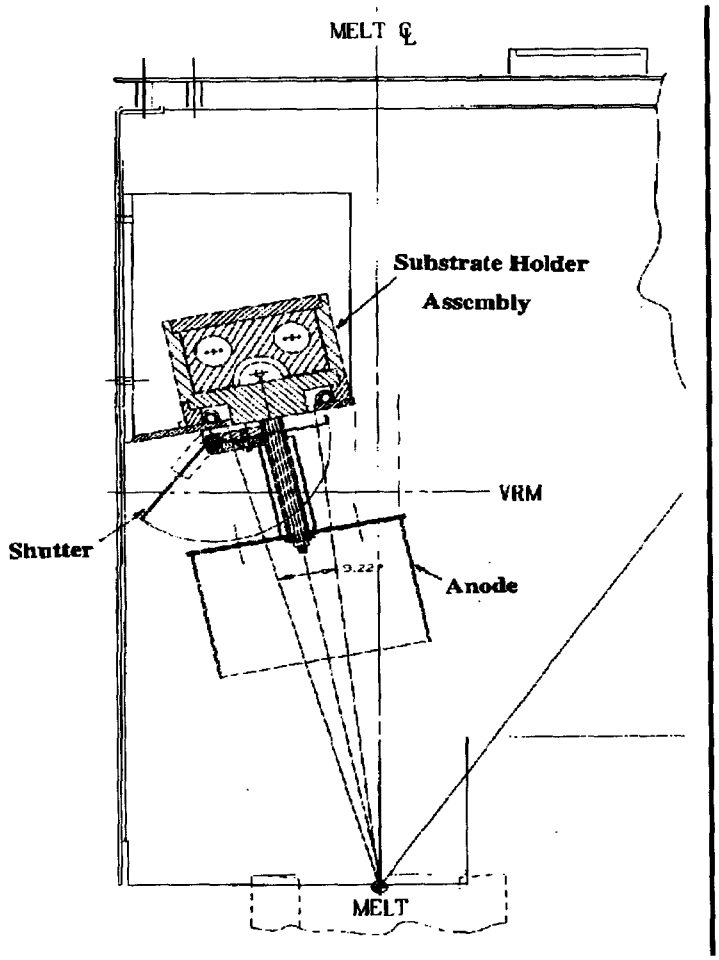


Figure 1 PVD Layout with Substrate Assembly and Ion-Enhancement Anode

Run #7 showed a very solid deposit with layers of sharp banding with columnar structure, similar to that of run #6 and 1000u of run #3. The tensile specimens from run #7 were heat treated (Gamma-quenched and aged) and tensile tested. They exhibited equivalent strength and ductility as the wrought-processed material (with strength of 130 ksi and 32% ductility).

A.3 Observations and Conclusions for PVD Process

We have characterized a wide range of process variables and broadened our PVD data base for U-6Nb forming, with the following observations:

1. Good deposits can be obtained:
   - 580°C, biased
   - 700°C, biased and ion-enhanced
   - 900°C and 1050°C, unbiased
2. questionable deposits:
   - 600°C and 700°C, unbiased
   - analysis not complete
3. Failed deposits:
   - 350°C, biased
   - 450°C and 480°C, unbiased

We conclude that the optimum PVD conditions have not been established.

Other process conditions, however, were established for the current melt chamber setup:

- adequate E-gun current is to be 4 - 6 amps at 35 kv
- maximum sustainable current the ion enhancement anode is 400amp at 40v
- manual controls of E-gun and feed are adequate
- substrate temperature is a function of location and E-gun power.

For future experiments, the deposition process variables can be improved with the following:

- a better substrate temperature control by using active heating and cooling, use of shutter and gun power adjustment.
- use of a close deposit surface temperature monitoring
- a close control of vapor flux between runs
- an better feed ingot conditioning to ensure deposit quality, and
- a better substrate surface finish definition

In conclusion, we have found that

- high purity, fully dense and fine grained materials can be consistently produced
- material property refinement can be made through PVD process and subsequent heat treatment
- heat treatment is critical
- tensile properties of PVD materials are comparable to those of wrought-processed material, based on the static testing results.

B.1 KEM Experiments

A schematic of the KEM system is shown in Figure 2. It consists of a supersonic nozzle for driving micron size particles to speeds in excess of 300 m/s and a recovery hood for recovering the over-sprayed powder. The gas source used two K-bottles of commercial grade helium and nitrogen, regulated to nozzle inlet pressures of 500 psig or less. The fluidizing gas pressure driving the feeder was regulated to a Δp of 20-30 psig above the process line

The test matrix consists of the following parameters with a wide range of values: powder materials, powder sizes (commercial grades), carrier gases (Helium and Argon), pressures, and substrate materials based on hardness, deposition thickness: thin film and bulk samples, as summarized in **Table B1**.

Figure 2 Schematic Representation of KEM System

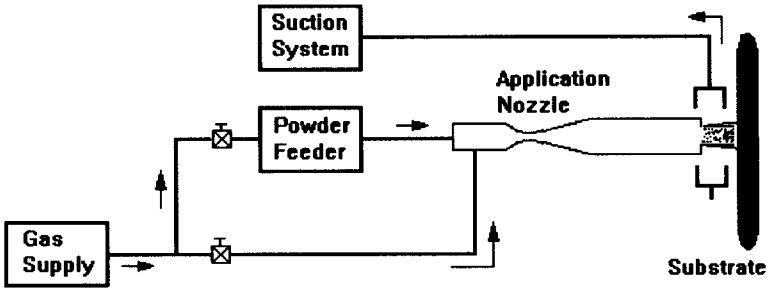
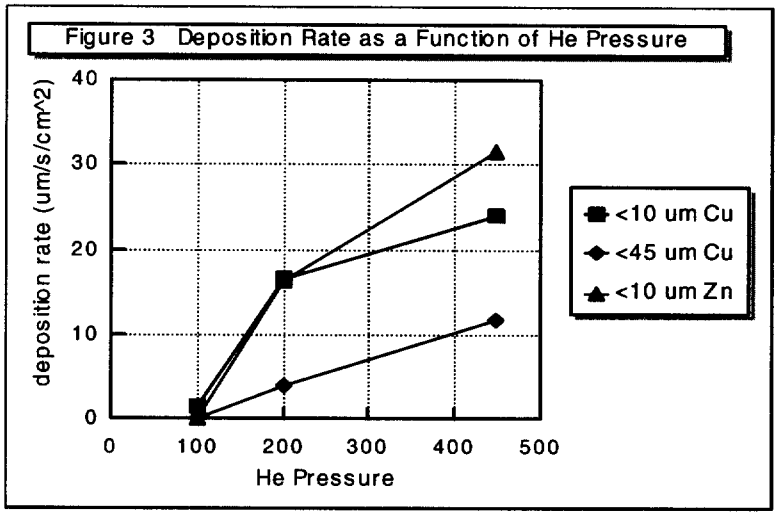


Table B1

Powder Material	Substrate	Gas Pressure	Data
Cu: <10 and < 45μm	Al	He: 100, 200, 450 psig	thin coating: deposition rates, hardness, metallograph
Cu: <10 μm	Ni	He: 450 psig	thin coating: hardness and metallograph
Zn: <10 and < 45μm	Al	He: 100, 200, 450 psig	thin coating: deposition rates, hardness; metallograph
Al: <10 and < 45μm	Al	He: 100, 200, 450 psig	thin coating: hardness and metallograph
Ni: <3μm	Al	He: 450 psig	thin coating: hardness and metallograph
Ti : < 45μm	Al	He: 450 psig	thin coating: hardness and metallograph
Cu<10μm	Al	He: 450 psig	bulk sample: metallograph, heat treatment, hardness, and mechanical testing
Zn<10μm	Al	He: 450 psig	bulk sample: hardness and metallograph
Ti<45μm	Al	He: 450 psig	bulk sample: metallograph, heat treatment, and hardness

B.2 KEM Results and Discussions

The thickness of the samples varies with the powder size and operating parameters. For example, up to 2.5 mm thick KEM deposition can be obtained with longer dwell time, smaller powder size and higher inlet pressure. Figure 3 compares the average deposition rates of Cu and Zn on Al substrate, in microns per second per cm^2, as a function of helium gas inlet pressure in psig, particle size, and depositing powder. These values are representative of the current KEM laboratory configuration consisting of a modified Metco powder feeder and a ITI-designed nozzle.



Comparison of deposition rates between different powders, e.g., Cu and Zn, can be difficult due to the effects of the feeder on the flow of powders. The large uncertainties associated with the deposition rates were attributable to powder flow rate variations that were highly dependent on the powder properties and the feeder behavior. Generally, higher inlet pressures and smaller particles, tended to increase the deposit rates, and samples with lower porosities and higher hardness. A few selected KEM depositions of various powders were made on substrates of copper and nickel.

The hardness measurements for Cu on Al and Zn on Al showed that the hardness tends to be slightly higher at the higher gas pressure for thicker spray-form buildup.

Table B2 summarizes the results for deposit on aluminum substrates, showing the effects of powder size, shape and gas pressure on the deposition rate, porosity, and hardness.

Table B2

Powder	Avg. Deposition Rate ($\mu m/cm^2$-s)	Helium Gas (psig)	Porosity	Hardness RH, 15T	Base Metal RH
Al (<10μm)	13 ± 7	200	<5%	71 ± 2	77 ± 2
Al (<10μm)	6 ± 5	450	<5%	72 ± 2	
Al (20μm), sph	99 ± 20	200	5-10%	61 ± 4	
Al (20μm), sph	384 ± 20	450	5-10%	64 ± 3	
Cu (<10 μm)	8 ± 3	100	<5%	77 ± 3	76 ± 1
Cu (<10 μm)	84 ± 17	200	5.6 ± 4.5	85 ± 2	
Cu (<10 μm)	122 ± 23	450	<5%	89 ± 2	
Cu (<45 μm)	20 ± 1	200	>10%	76 ± 2	
Cu (<45 μm)	59 ± 6	450	>10%	78 ± 3	
Ni (< 3 μm)	14 ± 5	200	-	88 ± 2	87 ± 1
Ni (< 3 μm)	23 ± 12	450	-	87 ± 2	(Inconel-600)

Ni (< 10 μm) Ni (< 10 μm)	13 ± 4 44 ± 7	200 450	5-10% -	88 ± 4 92 ± 1	
Ti (<45 μm) Ti (<45 μm)	29 ± 7 42 ± 13	200 450	18 ± 4.5 >10%	78 ± 3 83 ± 6	80 ± 1
Zn (<10 μm) Zn (10-25 μm)	82 ± 8 -- 160 ± 44 15 ± 6 -- 20 ± 3	200 - 450 200 - 450	<5% <5%	63 ± 4 58 ± 4	

Micrographic comparison of the particle size effects showed that the bulk and interfacial porosities were quite low (less than 5%) for the <10μm-Cu, while the <45μm-Cu exhibited moderate porosity (10-15%). The micrograph of a "Cu-on-Cu" deposit showed a much lower level of interfacial porosity, as compared to a "Cu-on-Al" deposit under otherwise the same conditions, suggesting that similar metals form stronger bonding than the dissimilar ones.

ITI generated the bulk (thick) samples (Cu, Ti, and Zn) [**Table B3**] using the parameters derived from the test matrix. All KEM bulk samples were fairly rough on the deposition side because of manually operated nozzle translation. The Cu and Ti bulk samples exhibited significant residual stress that resulted in bending of the samples. The zinc sample showed much less residual stress.

Table B3 Bulk sample deposition parameters:

Bulk Sample	Cu	Ti	Zn
Dimension	8.0cm x 1.6cmx 0.6cm	8.0cm x 1.7cm x 0.5cm	8.0cm x 1.8cm x 0.3cm
Powder Size	< 10 μm	< 45 μm	< 10 μm
Helium Pressure	300 psig	250 psig	300psig
Height of Curvature	3.0mm	2.5mm	0.5mm
Radius of Curvature	34	32	203

Table B4 Bulk samples test summary

	Treatment[1]	Rockwell Hardness[2]	Density	Tensile Property	Machineability	Oxygen Content
Cu	• As-deposited • Annealed	87 (15T) 80 (15T)	94% 96%	--- 38 ksi 0 .7% (ultimate)	poor good	0.209% ± 0.057 - comparable to general MSDS spec. for Cu powders
Ti	• As-deposited • Annealed • HIP'ed	82 (15T) 32 (C) 38 (C)	82% 93% 100%	--- --- ---	poor poor-fair fair	---
Zn	• As-deposited	74 (15T)	96%	---	fair	---

(1). Annealing condition: 2/3 melting temperature 3 hours; HIP condition: 15ksi at 1000°C 3 hours.
(2). [15T] is Rockwell superficial hardness: max. scale=92.5 equivalent to 19.9 on [C] scale.

The post-KEM processes included annealing of Cu sample, and annealing followed by HIP-ing of Ti sample. These treatments greatly improved the deposits mechanical properties. Table 4 is a summary of the analysis and testing results.

Annealing of KEM-deposited Cu had moderate reduction in porosity, (from 6% to 4%), and a slight decrease in hardness. Annealing and HIP-ing of the KEM-deposited Ti reduced the porosity from 17% to 0, increased the hardness greatly.

A tensile specimen machined from an annealed Cu sample was tested. The result shows that, with 38 ksi ultimate stress at 0.75% elongation, the specimen was brittle but relatively strong.

Elemental analysis of the Cu sample shows that the bulk oxygen content was in line with the level of commercial grade Cu powders, that the KEM process failed to purge out the oxide coating naturally occurring on the Cu particle surfaces.

B.3 KEM Summary

This study has demonstrated that it is feasible to use KEM process to deposit a wide range of metal powders to form both thin and thick coatings on various substrates. The work also has validated KEM as an efficient method for spraying fine reactive and pyrophoric powders such as titanium, in an inert gaseous atmosphere without using high vacuum deposition technology.

Post KEM processes such as annealing and/or HIP-ing will greatly improve the mechanical properties of the KEM-produced free-standing components. For refurbishment or thin coating applications the post-processes may not be as important.

The effect of the measured residual oxide on the KEM material property is not well understood. But it does suggest that powder conditioning and/or in-situ generation of powder as an integral part of the KEM process should be studied.

We have made preliminary modeling analyses of the KEM phenomena, and the results obtained to date reveal that impacts by solid particles at high velocities could cause deformations on both the incident particles and the target and that the deformation in the latter material is qualitatively similar to that seen in the test samples. A more detailed analysis of this work has been reported in: Final Report - FY96 Manufacturing Technology Thrust Area (DTED - A1-961016-CCya).

IV. Future Work

The proposed work for PVD and KEM should be separate:

PVD -

- optimizing the PVD process and post process variables
- forming and characterizing small cylindrical hydro-test specimens
- performing hydro-test
- studying other post-process treatments to optimize or tailor material property
- studying PVD process scale-up: geometry discontinuity and substrate design
- assessing weldability of the heat treated PVD alloy for microstructure and mechanical strength

KEM -

- carrying out particle-target interaction experiments
- U6Nb experiments
- powder synthesis and conditioning
- post-KEM processes
- process modeling analysis